

Nature of Nonclassical Bonds in Closo-Boranes: Nonlinear Population Analysis Approach

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ABSTRACT: The population analysis of higher order densities previously described by us and other investigators, has been applied to the description of 1,5-X₂B₃H₃ (X = N, CH, P, SiH, BH⁺) members of the closo-borane family. The calculated results, obtained at the SCF level, suggest the presence of three-center nonclassical bonds in the majority of systems studied. The good agreement between our results and those obtained from more sophisticated methods make this procedure a suitable and simple tool for detecting and localizing three-center bonds. © 1999 John Wiley & Sons, Inc. J Comput Chem 20: 1085–1090, 1999

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Introduction

The electronic structures of the closo-boranes $1,5\text{--X}_2\text{B}_3\text{H}_3$ ($\text{X} = \text{N}, \text{CH}, \text{P}, \text{SiH}, \text{BH}^-$) have been subject of controversy for some time.^{1–9} According to the reports of some investigators, these compounds constitute polyhedra of five vertices of type D_{3h} , with classical bonds among their atoms (Fig. 1). However, other researchers describe the presence of nonclassical structures for some members of that series, involving bonding interactions between the borons in the equatorial plane (Fig. 2). More recently, Schleyer and coworkers¹⁰ studied this family of compounds using *ab initio* computational determinations of bonding, energetic, and magnetic properties. Their conclusions point mainly to the existence of nonclassical structures.

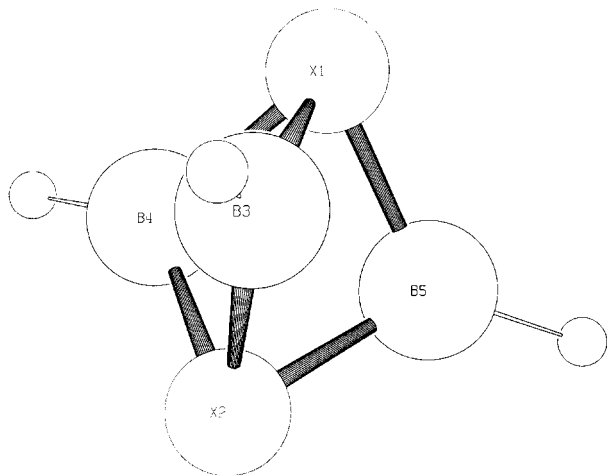


FIGURE 1. Classical structure of closo-boranes.

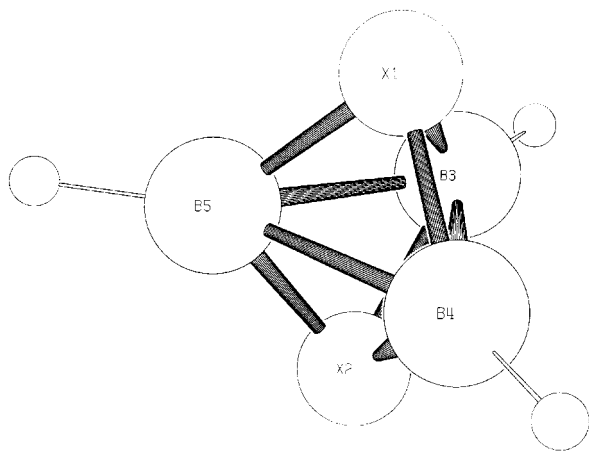


FIGURE 2. Nonclassical structure of closo-boranes.

Among the techniques addressed to provide a visualization of molecular electronic structures, a nonlinear population analysis has been reported that allows the detection and direct localization of multicenter bonds in molecules,^{11–14} as well as classical two-center two-electron ($2c\text{--}2e$) ones. The procedure is based on the idempotency properties of the first-order reduced density matrix at the SCF level and its relationships to other population analysis schemes has recently been discussed.¹⁵ Our technique carries out a partitioning of the total number of electrons N in a molecule, into mono-, bi-, and tri-atomic contributions, all these terms possessing a suitable physical meaning. This methodology has previously been applied to describe structures of some electron deficient carboranes¹⁶ and boranes,¹⁷ in which the presence of three-center bonds can be clearly detected, in good agreement with results arising from other treatments.

The main purpose of this study is to go beyond these reports and to extend the application of this approach to the description of other systems in which multicenter bonds could be expected to exist. Such an extension is necessary to test the reliability of this computational approach as a new tool of general application for the description of multicenter bonds in molecules. Another purpose of this study is to contribute to the existing debate about the nature of bonding in this interesting series of compounds.

The article is organized as follows. In the second section, the formalism of the population analysis used herein is briefly reviewed. In the third section the computational details are reported together with the discussion of actual numerical results.

Theoretical Background

Let us consider an N -electron system composed of n clamped nuclei, described at the closed-shell SCF level. If P is the spin-free charge and bond order matrix and S the overlap one related to the atomic orbital basis set $\{\alpha, \beta, \gamma \dots \omega\}$, the trace of the p th power of the (PS) matrix is:

$$\text{tr}(PS)^p = 2^{p-1}N \quad (1)$$

which is a consequence of the idempotency properties of the first-order reduced density matrix $(S^{\frac{1}{2}}PS^{\frac{1}{2}})$.¹⁸

Eq. (1) allows us to express the partitioning of the N electrons through contributions associated

with products of p elements of the matrix (PS):

$$N = \frac{1}{2^{p-1}} \sum_{\alpha} \sum_{\beta} \dots \sum_{\omega} (PS)_{\alpha\beta} (PS)_{\beta\gamma} \dots (PS)_{\omega\alpha} \quad (2)$$

which, for the particular case $p = 1$, leads to the well-known Mulliken population analysis¹⁹:

$$N = \sum_A \sum_{\alpha}^n (PS)_{\alpha\alpha} = \sum_A P_A \quad (3)$$

where A denotes a given nucleus and P_A is interpreted as the contribution of the atom A to the total number of electrons.

If we consider the case $p = 2$, eq. (2) allows us to obtain a partitioning of the N electrons into mono-, W_A , and biatomic contributions, W_{AB} :

$$\begin{aligned} N &= \frac{1}{2} \sum_{\alpha} \sum_{\beta} (PS)_{\alpha\beta} (PS)_{\beta\alpha} \\ &= \frac{1}{2} \sum_A W_A + \frac{1}{2} \sum_{A \neq B} W_{AB} \end{aligned} \quad (4)$$

The biatomic terms are identical to the so-called Wiberg indices, which are widely used as a measure of the classical bond order.^{20–22} A straightforward algebra explicitly presented in ref. 15 allows one to rewrite the eq. (4) in the alternative form:

$$N = \sum_A \left(Q_A + \sum_{B \neq A} W_{AB} \right) \quad (5)$$

where:

$$Q_A = P_A - \sum_{B \neq A} W_{AB} \quad (6)$$

is the unshared charge on atom A .²³

Further information can be obtained from the third power in eq. (2):

$$\begin{aligned} N &= \frac{1}{4} \sum_{\alpha} \sum_{\beta} \sum_{\gamma} (PS)_{\alpha\beta} (PS)_{\beta\gamma} (PS)_{\gamma\alpha} \\ &= \sum_A \Delta_A + \sum_{A < B} \Delta_{AB} + \sum_{A < B < C} \Delta_{ABC} \end{aligned} \quad (7)$$

in which a partitioning of N electrons into mono-, Δ_A , bi-, Δ_{AB} , and triatomic Δ_{ABC} contributions has been carried out. The main goal of the partitioning described by eq. (7), when compared with the partitioning expressed in eqs. (4) or (5), is that it opens up the possibility of detection of the eventual presence of three-center bondings in a molecule, through the terms of type Δ_{ABC} . Alternative

versions of these treatments have also been described^{12–16} in which normalization to $N/2$ rather than to N was used, but this change of normalization has no impact on the physical meaning of corresponding indices.

A simple algebraic manipulation of eqs. (3)–(7) allows one to establish relationships among the individual terms of the third power partitioning and those of lower powers; for details see ref. 15. The final relations are summarized in what follows:

$$\begin{aligned} \Delta_A &= \frac{1}{4} \sum_{\alpha}^A \sum_{\beta}^A \sum_{\gamma}^A (PS)_{\alpha\beta} (PS)_{\beta\gamma} (PS)_{\gamma\alpha} \\ &= Q_A + \frac{1}{4} \sum_{B \neq A} \sum_{C \neq A} I_{ABC} \end{aligned} \quad (8)$$

$$\Delta_{AB} = \frac{3}{2} W_{AB} - \frac{3}{4} \sum_{C \neq B} \sum_{B \neq A} I_{ABC} \quad (9)$$

$$\Delta_{ABC} = \frac{3}{2} \sum_{\alpha}^A \sum_{\beta}^B \sum_{\gamma}^C (PS)_{\alpha\beta} (PS)_{\beta\gamma} (PS)_{\gamma\alpha} = \frac{3}{2} I_{ABC} \quad (10)$$

The physical meaning of Δ_{ABC} terms is equivalent to that of the so-called three-center bond indices I_{ABC} .^{24–27} According to eq. (9), the biatomic terms Δ_{AB} and W_{AB} arising from the third and second power analyses, respectively, are equivalent only when nuclei A and B are not involved in any three-center bond in the molecule; that is, in this case, $\Delta_{AB} = \frac{3}{2} W_{AB}$. If this is not the case and some contaminating three-center terms participate, neither Δ_{AB} nor W_{AB} can be regarded as pure two-center bond indices due to the contaminating contributions of three-center bonding populations. The monoatomic terms, Δ_A , represent the unshared charge of atom A corrected by terms related to eventual three-center bonds (terms of type I_{ABC}) and two-center bonds (terms of type I_{ABB}) involving nucleus A .

The extension of the aforementioned partitioning to higher than third power in the (PS) products is also possible and the corresponding terms could analogously be used for the detection of multicenter bonding of higher than third order. However, we have not found any examples of systems with such kinds of bonding in our studies of population analyses involving boranes and some transition metal complexes. This, of course, does not mean that higher than three-center bonding cannot exist at all. In fact, it is true that, for example, the question of the existence of (6c–6e) bonding in aromatic systems could legitimately be raised and

the proof of the eventual existence of such type of bonding would be another interesting application of the aforementioned approach. This methodology is applied, in the next section, to the analysis of the nature of bonds in the closo-boranes family which, as pointed out in the Introduction, is still the subject of debate.

Before presenting the final results, however, it should be pointed out that, although the aforementioned formalism has been applied so far to closed-shell systems at SCF level of theory, the approach is not restricted to this particular level and the extension to open-shell systems will soon be published.²⁸

Results and Discussion

We have carried out quantitative evaluations of the terms, arising from the above reported partitionings, related to the mono-, bi-, and triatomic fragments of chemical interest in the members of the closo-boranes family $1,5\text{---}X_2B_3H_3$ ($X = N, CH, P, SiH, BH^-$). The calculations have been performed at the closed-shell SCF level using the program GAMESS-US²⁹ to generate the density matrix, which is then subjected to population analysis by our own computational implementation. The population analysis itself requires very little time as it takes only a few seconds for all systems studied. In all cases, the molecular geometries have been optimized completely. The basis sets used were 6-31G** except for the anion, which was described with the set 6-31++-. The results are summarized in Tables I–V where only values greater than 0.1 have been entered, except in the case of the I_{ABC} indices in the $Si_2B_3H_5$ molecule, where only the highest value has been included.

TABLE I.
Calculated Values of Mono-, Bi-, and Triatomic Contributions for $N_2B_3H_3$ Molecule.

Fragment	Q_A	Δ_A	W_{AB}	Δ_{AB}	I_{ABC}
N	4.540	5.120			
B	1.273	2.401			
H		0.248			
N—N				0.113	
N—B			0.961	1.285	
B—B			0.266	0.200	
B—H			0.964	1.437	
B—N—B					0.124

TABLE II.
Calculated Values of Mono-, Bi-, and Triatomic Contributions for $C_2B_3H_5$ Molecule.

Fragment	Q_A	Δ_A	W_{AB}	Δ_{AB}	I_{ABC}
C	2.531	3.380			
B	1.310	2.434			
H (X group)	−0.108	0.159			
H		0.271			
C—H			0.943	1.422	
C—B			0.976	1.295	
B—B			0.288	0.230	
B—H			0.958	1.433	
B—C—B					0.127

TABLE III.
Calculated Values of Mono-, Bi-, and Triatomic Contributions for $P_2B_3H_3$ Molecule.

Fragment	Q_A	Δ_A	W_{AB}	Δ_{AB}	I_{ABC}
P	11.908	12.674			
B	1.589	2.616			
H		0.238			
P—P				0.207	
P—B			0.938	1.241	
B—B			0.340	0.346	
B—H			0.964	1.438	
B—P—B					0.122

TABLE IV.
Calculated Values of Mono-, Bi-, and Triatomic Contributions for $Si_2B_3H_5$ Molecule.

Fragment	Q_A	Δ_A	W_{AB}	Δ_{AB}	I_{ABC}
Si	9.973	10.969			
B	1.827	2.697			
H (X group)		0.314			
H		0.262			
Si—H			0.949	1.424	
Si—B			0.983	1.422	
B—B			0.130	0.119	
B—H			0.963	1.437	
B—Si—B					0.041

These results show that all members of the series (except for $Si_2B_3H_5$) feature low but non-negligible values for the Wiberg indices, W_{BB} . This means that some kind of partial bonding between the equatorial borons exists in these molecules. According to our experience, such “partial” bonds, with fractional orders between classically non-bonded atoms, are characteristic of the presence of multicenter bonding. To prove the expected pres-

TABLE V.
Calculated Values of Mono-, Bi-, and Triatomic Contributions for $B_5H_5^-$ Anion.

Fragment	Q_A	Δ_A	W_{AB}	Δ_{AB}	I_{ABC}
B (X group)	1.443	2.493			
H (X group)	0.502	0.587			
B	1.398	2.542			
H	0.474	0.605			
B(X)—H(X)			0.905	1.384	
B(X)—B			0.952	1.219	
B—B			0.461	0.465	
B—H			0.903	1.394	
B—B(X)—B					0.152

ence of nonclassical multicenter bonding, the above systems were subjected to the population analysis described by eq. (7). As can be seen in the tables, some triatomic contributions do indeed have significant values that cannot be neglected, in order to explain the loss of the $\frac{3}{2}$ proportionality between the Δ_{BB} and W_{BB} values, as well as between the Δ_{BX} and W_{BX} ones, related to the third component, X, of the three-center bond [see eq. (9)]. These triatomic contributions, together with some biatomic ones, can also explain, according to eq. (8), the differences between the Q_A and Δ_A ($A = N, C, P, Si, B$) values. The nonnegligible triatomic contributions are localized specifically in the fragments B—X—B, constituted by two equatorial borons and the heavier atom in the X group. This result is very interesting because this is the same molecular fragment in which nonclassical ($3c-2e$) bonding was detected in previous studies, especially in ref. 10. We can thus see that, despite its relative simplicity, the above approach is able to confirm the results of even much more sophisticated techniques and can thus be used advantageously as a new efficient tool for the study of systems with complex bonding patterns.

It is also of interest to point out that the Δ_{BH} and W_{BH} indices attain, in all these compounds, values close to the ideal limits and keep to the $\frac{3}{2}$ relation rather well, so that the B—H links can be described as classical ($2c-2e$) Lewis bonds. Similar comments can be applied to the Δ and W indices corresponding to the bonding into the X group (in the case of $X = CH, SH, BH^-$). These results confirm previous observations¹⁷ in the sense that, when a three-center bond is present in a molecule, it has a localized character, so that the rest of the molecule can be generally described by classical ($2c-2e$) bonds.

Another conclusion that can be deduced from our results concerns the relative strength of three-center bonding in the studied series of compounds. Because it is possible to see, quite in keeping with the well-known tendency of boron to form three-center bonds, the strongest nonclassical bonding is observed for $X = BH^-$. Slightly weaker three-center bonds are then found for $X = C$ and N and the final order $BH^- > C > N$ of the strength of multicenter bonding again agrees with previously reported results.¹⁰

However, the same order is not observed for the second row elements, where $Si_2B_3H_5$ presents the lowest three-center character of all members of the series. Thus, for instance, if we compare this value with the limiting value of 0.37 derived from the idealized analytical model,¹³ it is evident that the three-center character of bonding is indeed very weak in this molecule. This result is of much interest because the same conclusion about the low nonclassical character of bonding in $Si_2B_3H_5$ was also obtained by investigators.⁷⁻⁹ We can thus conclude that, while in a majority of studied closoboranes the structure is better described by a model of nonclassical three-center B—X—B bonds (Fig. 2), the case of the silicon analog is a bit different and its structure is rather consistent with the classical model of localized two-center bonds (Fig. 1). Summarizing the results, it is possible to conclude that the third-order population analysis scheme described by eq. (7) constitutes a suitable and very simple procedure for providing a visualization of the bonding molecular patterns, which gives enough information to detect and localize the nonclassical bonding nature in the closoboranes family.

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